

DEVELOPMENTS IN SIMULATION METHODS FOR SOLID CATALYSTS

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INTRODUCTION

The complexity of most heterogeneous catalyst systems has traditionally hampered the effective application of computer simulation methods. However, increasing sophistication in methodology and application, coupled with the development of tools specifically tailored for solid catalyst systems is now enabling computer modeling to address a number of problems encountered during the development and implementation of a variety of heterogeneous catalysts. We outline here some of our recent progress in this area, and give specific examples taken from (1) the characterization of crystalline catalysts and supports (2), the development and dynamical simulation of metal atoms and clusters on amorphous inorganic matrices (3), the dynamical behavior of hydrocarbons within microporous media and (4) the application of quantum chemical tools to studying local coordination environments and chemistries. In-depth theoretical studies of reaction pathways over real, multicomponent heterogeneous catalysts at process conditions remain a far distant goal, but, as the present examples demonstrate, considerable insight can be gleaned when tailored tools and approaches are applied to appropriately phrased heterogeneous catalyst problems.

CATALYST CHARACTERIZATION

Structural characterization is a key step in the development of a fundamental understanding of catalyst function. Most real heterogeneous catalyst systems are, however, complex and do not lend themselves readily to study by conventional structural characterization tools. Microporous crystals such as zeolites, the basis for current fluid cracking catalysts, and mixed metal oxides of interest in a wide range of oxidation reactions are microcrystalline. Powder X-ray diffraction techniques are therefore a key source of structural data. Powder diffraction data can, using the Rietveld method, be the basis for refinement of an approximate model, but the derivation of the initial model is often difficult. Computer simulations can greatly facilitate the structure solution process, either by direct derivation of an initial model from unit cell and compositional data, combined with established geometrical constraints (1), or by enabling a developing structural model to be manually adjusted while the degree of match between the simulated powder diffraction pattern and that observed is interactively monitored (Figure 1) (2, 3).

AMORPHOUS SUPPORTS

Heterogeneous catalysts are rarely used in a 'neat' form and in many cases the catalyst support or binder can play a significant role in processes. For example, classical reforming catalysts, or a large number of hydrogenation catalysts are comprised of metals dispersed on non-crystalline supports. In such cases a direct determination of structure from scattering data is not possible. Computer simulations can, however, be used effectively to develop models for the surfaces of amorphous

matrices, such as silica (4), and to study the dynamical interactions of metal atoms and clusters with such a support (Figure 2) (5, 6).

HYDROCARBONS WITHIN MICROPOROUS CRYSTALS

The behavior of hydrocarbons within microporous crystals such as zeolites is central to the role of zeolites as catalysts and sorbents. A number of experimental tools can be applied to studying the preferred sites occupied by sorbed hydrocarbons within zeolites, and aspects of the character of the hydrocarbon molecular motion over several time-scales (7). Modeling is already being applied in studies of sorbate location and diffusion (e.g. (2, 8, 9)), and computer simulations will clearly play an increasingly important role as the mechanism by which the experimental insights provided by these various methods can be combined into a self-consistent picture of the zeolite - hydrocarbon interactions. Key areas for development are the potential functions and parameters used in describing the interatomic interactions, and methods for simulating dynamical phenomena that occur on characteristic time scales longer than a few thousand picoseconds for which classical molecular dynamics methods are currently unviable.

APPLICATIONS OF QUANTUM CHEMICAL METHODS

Quantum chemical methods must play a central role in developing an understanding of catalyst reactivity. However, the complexity of real catalysts that hampers the application of structural characterization methods also imposes restrictions on the degree to which quantum chemical methods can be applied to models that approximate actual catalyst centers. Methods are continually being refined and *ab initio* Hartree-Fock calculations on a complete sodalite cage have recently been described (10). *Ab initio* methods have also contributed considerably to our understanding of Brønsted acidity in zeolites and to the geometries of such active sites (11, 12). Additionally, *ab initio* methods provide a powerful means of computing potential energy surfaces and of hence deriving potential energy functions and parameters for both intra- and intermolecular interactions.

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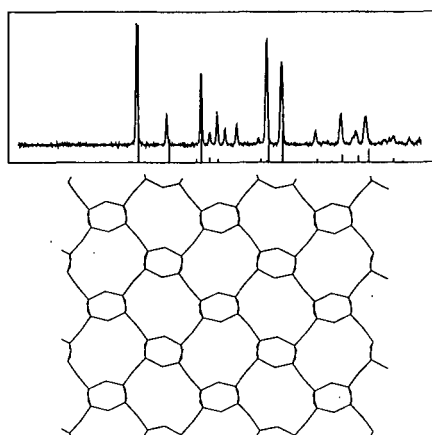


Figure 1: A model of the zeolite ABW-framework drawn as straight lines connecting adjacent Si or Al sites and their coordinating oxygen atoms (lower). The powder X-ray diffraction pattern computed interactively as the structure is edited is shown above as bars, compared with the experimental pattern of an ABW-framework material (continuous line) (3).

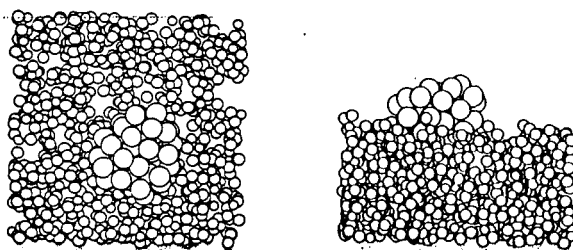


Figure 2: Top (left) and side (right) views of a model Pt cluster on a vitreous silica support generated by a series of molecular dynamics simulations (5, 6).